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United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Cincinnati OH 45268

Research and Development

EPA-600/S2-81-130 Oct. 1981

EPA

Project Summary

Nickel Recovery from Electroplating Rinsewaters by Electrodialysis

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A program to demonstrate the feasibility of metal salt recovery and pollution control on a Watts-type nickel plating line by electrodialysis was conducted at Risdon Manufacturing Co., Waterbury, CT. Each of two reclaim rinse tanks, arranged in series following plate tanks, was treated by recirculating the rinse solutions through separate electrodialysis stacks. The first rinse solution was maintained at 2-5 g/l nickel and the second rinse held at 0.3-0.4 g/l nickel over several months of plating operations. The nickel salts recovered from the rinse solutions were concentrated 20-fold by the electrodialysis treatment and could be returned directly to the plate tanks for reuse. Several operational problems are discussed and recommendations made. It is concluded that electrodialysis can be a useful and economically viable process for the treatment of at least some types of electroplating rinses. Both plating-metal recovery and pollution control are accomplished.

A cost estimate based on the data obtained during the demonstration indicates that 95% of the nickel lost from untreated rinses could be recovered and that ancillary benefits in sludge disposal, use of treatment chemicals, etc. could be realized. Payback periods of less than 18 months are anticipated for commercial units.

This report was submitted in fulfillment of Grant No. R803742 by Risdon Manufacturing Co. under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period June 1, 1975 to December 31, 1976, and work was completed as of February 22, 1977.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Electrodialysis (ED) is a membrane process that can be used for the separation, removal, or concentration of ionized species in water solutions. These operations are accomplished by the selective transport of ions through ion-exchange membranes under the influence of an electrical potential applied across the membrane. Ion-exchange membranes, permeable to either anions or cations, but not both, are thin sheets of ion-exchange material normally reinforced by forming on a synthetic fabric backing. They range between 0.1 to 0.6 mm in thickness and are available in standard sheets up to 1 x 1.5 meters. As in the case of particulate ion-exchangers, the resin matrix is usually copolymerized styrene-divinylbenzene, and exchange capacity is imparted by sulfonic acid groups (cation-selective membranes) or

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quaternary ammonium or pyridinium groups (anion-selective membranes). The terms cation-exchange, cation-selective, and cation-permeable are used interchangeably in membrane terminology as are the corresponding terms anion-exchange, anion-selective and anion-permeable.

In the usual configuration employed for ED, hundreds of alternating anion-selective and cation-selective membranes are arrayed in parallel between two electrodes to form an ED multicell or "stack." Specially designed spacer/gaskets separate the membranes by forming leak-tight, flow-directing compartments or cells between adjacent membranes. The solutions to be treated are distributed to and collected from these cells by two internally manifolded hydraulic circuits, one for the ion-depleting or diluting cells and one for the alternating ion-receiving or concentrating cells. The repeating stack unit of a cation-selective membrane, a diluting spacer, an anion-selective membrane, and a concentrating spacer is termed a cell-pair, and the size and demineralizing capacity of ED equipment can be characterized by indicating the number of cell-pairs comprising a multicell.

The passage of a direct current through the ED stack causes the anions and cations in the raw process solution fed to the diluting cells (the feed) to move in the direction of the anode and cathode, respectively. Because of the alternating membrane arrangement they leave the diluting cells and accumulate in the concentrating cells. This process is shown schematically in Figure 1 where the concentrating cells are odd numbered and the diluting cells have even numbers. As indicated, positive cations are attracted to the negative cathode and pass from the diluting compartments, through the cation-selective membranes forming the cathode side of the cell, into the concentrating compartments where they accumulate, since their further transport is prevented by anion-selective membranes on the cathode side of the concentrating cells. Anions move in the opposite direction, passing through the anion-selective membranes and being excluded by the cation-selective membranes. The partially deionized effluent from the diluting cells may be suitable for use after a single pass through the stack or recirculated for further demineralization. The solution introduced to the concentrating cells is usually the same process stream as that fed to the diluting cells, but only 20-25% of its volume, and is eventually discarded at 3 or 4 times the original concentration having acquired the ions removed from the solution passing through the diluting cells. A separate solution, which may also be drawn from the raw stack feed, is used to rinse the electrode compartments and remove the gases formed by the electrode reactions. It may be recirculated or pumped on a once-through basis and is usually acidified to prevent scaling. Use of the multi-

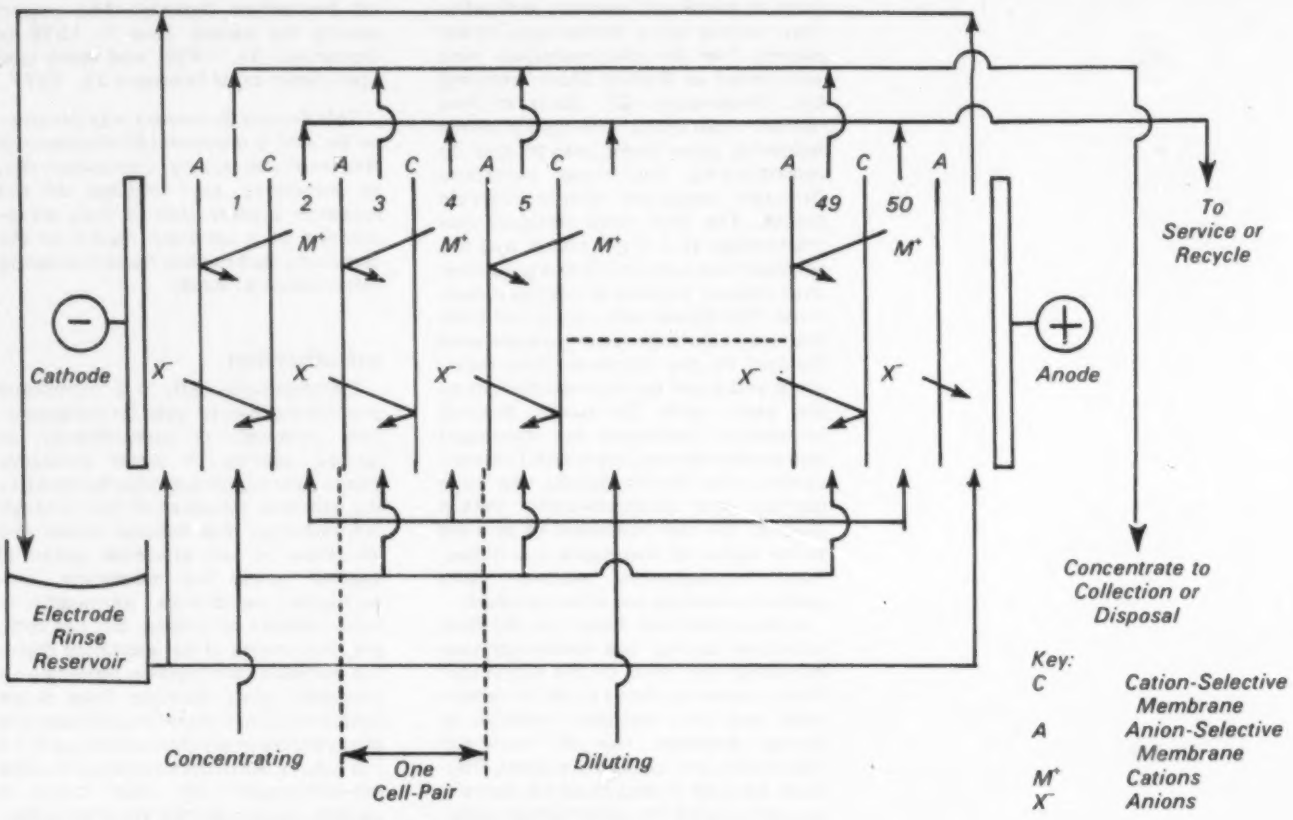

Figure 1. *Electrodialysis multicell schematic.*

cell concept makes it possible to obtain a deionizing effect equal to many times the electrical equivalents passed between the electrodes.

In the late 1940's, the development of highly selective and physically strong synthetic ion-exchange membranes made feasible commercial application of the ED multicell. The first and still largest use of ED is for desalinization of brackish water; the second major application is de-ashing whey. Besides these now conventional uses, in which the desired product is the deionized feed to the diluting cells, an interesting and important application of ED is the deliberate use of the concentrating steam to concentrate and recover ionic constituents from the waste or process water fed to the stack. In this modification the recovered concentrate can also be considered a product solution from the ED treatment, and the recovered material is available for reuse in the original process or for further treatment and/or disposal. In the latter case subsequent handling of the recovered solution is substantially simplified, since it is typically 1-2% of the original volume. Electrodialytic concentration of seawater is widely used in Japan in conjunction with solar evaporation to produce table salt and has great potential utility in the electroplating and metal finishing industries both for pollution control and metal recovery. The Japanese have extended their work on concentration by ED to exploratory studies on waste liquors from copper and nickel plating operations, and laboratory tests in this country have also indicated the possibility of electrodialyzing nickel solutions (Figure 2). Another recent laboratory investigation has looked at the ED of a copper cyanide plating bath rinse for recovery of plating chemicals and elimination of toxic discharges. Our own preliminary studies have indicated that nickel can be recovered as a valuable product solution from a simulated plating rinse bath at many times its concentration in the bath by using especially designed ED multicells and appropriate operating conditions. Based on these laboratory data, a prototype ED unit was constructed for a field test and demonstration program at Risdon Manufacturing Co.

Conclusions

The field test program demonstrating the recovery of nickel from plating bath rinse waters by ED has shown that ED can be a useful and economically viable process for the treatment of at least some types of electroplating rinses, specifically those from Watts-type nickel plating lines. The process is capable of reducing nickel content in plating line effluents to the ppm range, can recover 95% of the nickel salts lost with conventional rinsing techniques and substantially reduce other raw material usage, can minimize the effort and space required for operation of standard destruct equipment, and can return a concentrated nickel solution directly to the plate tanks.

ED treatment of a reclaim rinse immediately following the nickel plate tanks held the rinse concentration at 2-3 g/l nickel. A second reclaim tank in series with the first was maintained at approximately 0.3 g/l nickel. Lower concentrations appear to be easily attainable with appropriate equipment sizing. Metal losses via drag-out to the destruct system following the reclaim rinses were drastically reduced compared to those expected with a countercurrent or unmodified reclaim rinsing sequence. For plating operations similar to the demonstration line yearly savings are estimated to be at least $16,000 in raw materials with a concomitant decrease of about 2,300 kg (5,000 lb.) in sludge from pollution control facilities. Net cost savings should increase as chemicals become more expensive and pollution regulations more stringent. Depending on the operation of the plat-

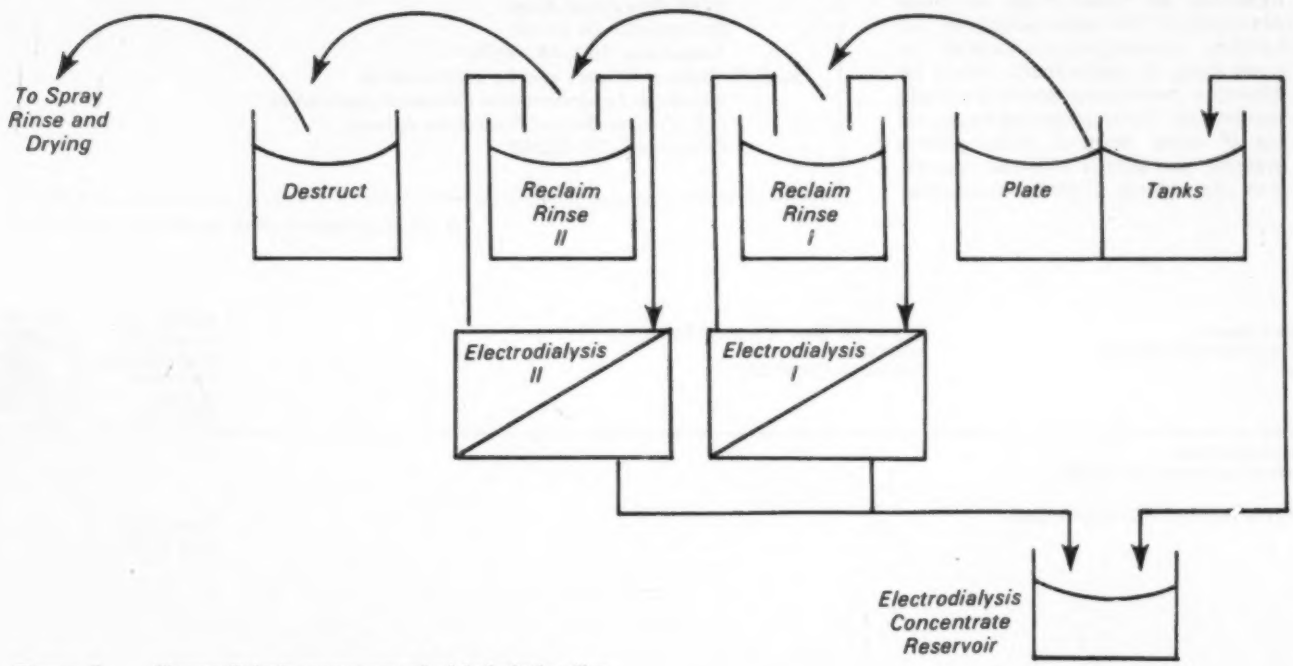

Figure 2. Electrodialysis treatment of nickel plating line.

ing line, additional savings may be realized on water usage, storing and handling of chemicals, improved rinsing, and additive recovery.

In contrast to reverse osmosis, ED can concentrate the nickel 50- to 100-fold, permitting direct return to the plating solutions without the necessity of an extra evaporation step or increase in plate tank evaporation rate. The membranes employed are mechanically stronger and more resistant chemically than typical reverse osmosis membranes. The concentration of the reclaim rinse can be held at any desired value and the recovery rate adjusted to remove nickel to match any drag-out rate. ED is a continuous process and requires no interruption for regeneration for ion-exchange material or disposal of regenerating solution as do conventional ion-exchange systems.

The program has also demonstrated that maintenance and operation of ED equipment by plating room personnel are completely satisfactory with a minimum of training. Other than for start-up and shut-down procedures only intermittent attention by the operator is required and much of his time can be spent on other duties.

Recommendations

The success of the electrodialytic treatment of nickel rinse solutions described in this report suggests that further investigations aimed at broadening its applicability would be desirable. Recommendations are made that demonstration programs be carried out on other types of nickel plating systems, particularly on those systems that use organic brighteners or other classes of additives not employed on the test line at Risdon. Extension of the technique to additional plating solutions, i.e., copper and chromium, would be of considerable interest. Simple salt or "acid" baths are the obvious choices for initial efforts. Demonstration of ED on plating lines using countercurrent rinsing and/or automatic barrel handling would also be valuable in estimating the potential savings (Table 1) and in water and space requirements, in defining system versatility, and in generalizing experience with the process. Improved maintenance schedules and more accurate estimates of costs and component life would be developed.

At least two employees familiar with the individual plating operation should be trained in ED technology to insure full-time monitoring capability. Responsibility for the ED equipment must be recognized as an integral part of their job and an appropriate percentage of their time assigned to recovery operations. Adequate filtration of the influent to the ED stack is a required pretreatment, and some cooling may be necessary. Wide fluctuations in ambient temperature should be avoided. Besides the safety precaution in the interconnection of the stack current/feed pump circuitry, additional DC cutoffs based on flow attenuation and feed conductivity are desirable.

Table 1. Estimated Operating Costs for 50 Cell-Pair Nickel Recovery Unit (1976 Dollars)

	$/day	$/year
Electric power	.70	168
Labor	3.75	900
Chemicals	.02	5
Filter cartridges	.91	219
Replacement membranes	1.25	300
Total	$6.63	$1592

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***Fred Ellerbusch** and **Mary K. Stinson** are the EPA Project Officers (see below).*
The complete report, entitled "Nickel Recovery from Electroplating Rinsewaters by Electrodialysis," (Order No. PB 81-227 209; Cost: $8.00, subject to change) will be available only from:
National Technical Information Service
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